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ABSORPTION OF MICROWAVES IN SOLUTIONS OF ORTHO-CHLOROPHENOL*

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ABSTRACT. The absorption of 3.18 cm microwaves in solutions of *o*-chlorophenol in CCl_4 has been studied using optical method. It has been found that the 15% solution exhibits maximum absorption at 0°C and the 7 5% solution shows the maximum at −13°C. The aggregate absorption is found to increase with lowering of concentration. These results have been discussed in the light of those observed in the investigations on the infra-red and Raman spectra of solutions of the compound in different solvents reported by previous workers. It has been concluded that in dilute solution in CCl_4, the OH group in most of the molecules possesses freedom of rotation

INTRODUCTION

The Raman spectra of solutions of *o*-chlorophenol in different solvents have been studied by Mukherjee (1958) and it has been observed that the intensity of the line 3533 cm^{-1} increases when the liquid is dissolved in the solvents and it increases further when the concentration is diminished from 30% to 15%. He pointed out that as this line is assigned to the OH valence oscillation in the molecule with the OH group in the *trans*-position, such molecules become predominant in very dilute solutions. He further pointed out that the assignment made by Pauling (1936) of the strong infrared absorption peak at 6910 cm^{-1} in CCl_4 observed by Wulf and Liddel (1935) is probably not correct. More recently, Sirkar, Deb and Banerjee (1958) from an investigation on infrared spectra of the solutions of *o*-chlorophenol concluded that in dilute solutions most of the molecules have the OH group in the *trans* configuration. They observed that the spectrum due to pure *o*-chlorophenol in the liquid state consists of three broad absorption maxima indicating the presence of large number of double-molecules as suggested by Pauling (1945) and also some molecules of *cis* and *trans* configurations. Similar conclusions were also arrived at by Roy (1958) who studied the electronic spectra of *o*-chlorophenol in different solvents at different temperatures.

The absorption of 3.18 cm microwaves in *o*-chlorophenol and *p*-chlorophenol was studied by Ghosh (1955*a*) who found that although *p*-chlorophenol shows absorption in the range 50°C—170°C with the maximum at 85°C, *o*-chlorophenol

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does not show any absorption throughout the temperature range from the freezing point up to the boiling point of the substance. He explained this by assuming that most of the molecules in the liquid state are of the *cis* form.

The results of the investigations on the Raman spectra and the infrared absorption spectra of solutions of *o*-chlorophenol mentioned above indicate, however, that the OH group has freedom of rotation in some of the molecules in the solutions. In that case such solutions should exhibit absorption of microwaves at proper concentrations and temperatures to produce proper values of coefficient of viscosity. The present investigation was undertaken to find out whether such absorption takes place in the 3-cm region.

EXPERIMENTAL

The experimental arrangements and the method of determining absorption maxima were similar to those used by Ghosh (1954*a*). A klystron oscillator of the type 793A was used as the source of microwaves of frequency 9415 Mc/sec.

Chemically pure samples of *o*-chlorophenol and carbon tetrachloride were dehydrated and fractionated. Proper fractions were collected and redistilled under reduced pressure. Solutions with 15% and 7.5% molar concentrations of *o*-chlorophenol in CCl_4 were used. In the case of 15% solution the absorption was studied in the temperature range from 40°C to about −20°C. The solution was diluted to 7.5% and its temperature was lowered up to −50°C in order to find out the temperature at which maximum absorption takes place in this case. The values of the static dielectric constant, refractive index and the coefficient of viscosity were required for the calculation of the radius of the rotor. These data of the solutions of *o*-chlorophenol in CCl_4 were not available in the standard literature. The dielectric constant was measured in the laboratory. A tuned circuit with a special type of cell connected parallel to a standard condenser was loosely coupled to the coil of a constant frequency oscillator. The cell used for this purpose consists of a gold plated brass cylinder placed coaxially inside another hollow gold plated cylinder and the inner cylinder is kept insulated from the outer one with the help of a polystyrene cap. The thickness of the annular space between the cylinders is 3 mm.

The values of coefficient of viscosity η of the solutions at the required temperatures were calculated from the formula $\eta = x_1\eta_1^{\frac{1}{3}} + x_2\eta_2^{\frac{1}{3}}$, where x's and η's are the mole-fractions and coefficients of viscosity of the pure components at the temperature concerned. The coefficients of viscosity of pure *o*-chlorophenol and pure carbon tetrachloride were obtained by extrapolating the data given in the International Critical Tables.

From the refractive indices of the pure substances, the refractive indices of the solutions were calculated by using the standard formula.

RESULTS AND DISCUSSION

The coefficient of absorption μ was calculated from the formula :

$$\mu x = \log_e(I_0/I)$$

where x is the thickness of absorption cell and I_0/I is the ratio of the currents in the detector without and with the cell in its position respectively. The values of log I_0/I plotted against temperature of the 7.5% and 15% solutions are shown in the two curves reproduced in figure 1.

The maximum absorption in 15% solution takes place at 0°C and that for 7.5 % occurs at −13°C for microwaves of frequency 9415 Mc/sec. The relaxation time τ was calculated from Debye's equation .

$$\omega\tau = \frac{\epsilon_0 + 2}{\epsilon_1 + 2}\sqrt{\frac{\epsilon_1}{\epsilon_0}}$$

where ϵ_1 is the static dielectric constant of the solution and ϵ_0, the dielectric constant of the solution at frequencies in the optical range which was taken to be the square of the refractive index n of the solution at 20°C for sodium D-line, as the values of refractive indices at lower temperatures were not available.

The value of the radius a of the rotor was calculated from Debye's equation

$$a^3 = \frac{\tau KT}{4\pi\eta}$$

where η is the coefficient of viscosity at the temperature T°K. The values of a and the constants used in the calculation of a are given in Table I.

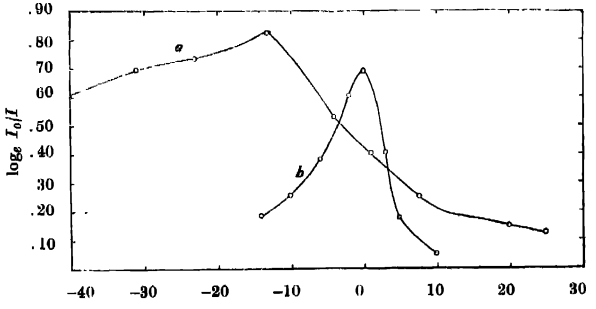

Fig. 8. Absorption of 3.18 cm microwaves in solution of o-chlorophenol in CCl_4.
Curve A – 7.5% solution (molar concentration).
Curve B – 15% „ („).

TABLE I

Molar Concentrations of *o*-chlorophenol in CCl_4 sol.	Temp. for maximum absorption in °K	Static dielectric constant of sol.	n	$\eta \times 100$	$\tau \times 10^{11}$ (in sec.)	$a \times 10^8$(cm)
15%	273°K	3.71	1.47	1 9	1.67	1.39
7.5%	260°K	2.60	1.47	2.7	1.63	1.43

It can be seen from figure 1 that the solution of *o*-chlorophenol exhibits absorption in 3-cm microwave region. The maximum absorption occurs at −13°C for the 7.5% solution and that for the 15% solution occurs at 0°C. The peak of the curve for 7.5% is higher and much broader than the peak of the other curve. The radius of the rotor calculated by using Debye's formula is found to be approximately 1.4 Å in both the cases. It is of the same order as that of the freely rotating OH groups observed by Ghosh (1954*b*; 1955*b*,*c*) in phenols and alcohols

Ghosh (1955*a*) did not observe any absorption of 3.18 cm waves in pure *o*-chlorophenol throughout the temperature range from the freezing point to the boiling point of the liquid. He concluded that most of the molecules have their OH group in *cis* position with respect to the chlorine atom of the same molecule in the pure liquid. The results of the present investigation, however, show that in solutions of *o*-chlorophenol in CCl_4 the OH group is free in some of the molecules and the radius of the rotor is found to be of the same order as that of the freely rotating OH group. It is, therefore, clear that hydrogen atoms of OH groups in the molecules of *o*-chlorophenol in solutions in CCl_4 are not chelated as observed by Ghosh (1955*b*) in pure liquid. The fact that the peak of the curve for 7.5% solution is higher and broader than that of the other curve indicates that the intensity of absorption is higher for 7.5% solution than for the 15% solution. Hence the number of molecules with free OH group is greater in 7.5% solution than that in 15% solution. Thus the observations in present work suggest that the OH group in most of the molecules of *o*-chlorophenol in dilute solution in CCl_4 possesses freedom of rotation about an axis coinciding probably with the diameter of benzene ring passing through the carbon atom to which the OH group is attached. This further shows that in the dilute solutions of *o*-chlorophenol in CCl_4, a predominantly large number of molecules of *o*-chlorophenol have their OH groups turned to the *trans*-position with respect to the chlorine atom by the influence of the solvent molecules.

Mukherjee (1958) concluded from the results of investigation on the Raman spectra of the solutions of *o*-chlorophenol in different solvents, that the OH group is free in most of the molecules in the solution. Sirkar, Deb and Banerjee

(1958) investigated the infra-red absorption spectra of the solutions of *o*-chlorophenol in carbon tetrachloride and cyclohexane of different strengths and also of the pure liquid. In the case of pure *o*-chlorophenol they concluded from the results that there are some dimers in the liquid as proposed by Pauling (1945) and the feeble absorption produced in the region 3500 cm^{-1}—3600 cm^{-1} might be due to OH oscillation in a small percentage of single molecules of *trans*-configuration. They further observed that with the change of concentration from 30% to 5% the number of such single molecules of *trans* configuration increases rapidly. The results of the present investigation corroborate the conclusions drawn by the above workers, because at the lower concentration the aggregate absorption is much larger than that in the 15% solution.

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REFERENCES

Ghosh, D. K., 1954*a*, *Ind. J. Phys.*, **28**, 191.
,, 1954*b*, *Ind. J. Phys.*, **28**, 485.
,, 1955*a*, *Ind. J. Phys.*, **29**, 450.
,, 1955*b*, *Ind. J. Phys.*, **29**, 161
,, 1955*c*, *Ind. J. Phys.*, **29**, 581.
Mukherjee, D. K., 1958, *Ind. J. Phys.*, **32**, 192.
Pauling, L., 1936, *J. Am. Chem. Soc.*, **58**, 94.
,, 1945, Nature of Chemical bond, p. 324.
Roy, S. B., 1958, *Ind. J. Phys.*, **32**, 525.
Sirkar, S. C., Deb, A. R. and Banerjee, S. B., 1958, *Ind. J. Phys.*, **32**, 345.
Wulf, O. R. and Liddel, U., 1935, *J. Am. Chem. Soc.*, **57**, 1464.